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Surface Properties Contrast between Al Films and TiO_2 Films Coated on Magnesium Alloys by Magnetron Sputtering

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Al films and TiO_2 films were separately coated on AZ31 magnesium alloy substrates by means of magnetron sputtering method. The surface properties of the samples were explored and compared. Scanning electron microscope (SEM) observed the compact structure characteristics of as-deposited Al films and TiO_2 films. After heat treatment under 200ºC for half an hour the films kept the compact structure characteristics and there didn't exist structural defects on the surface of the films. Nano-indentation measurement results display that the micro-hardness of as-deposited Al film and TiO_2 film reaches about 1.90 Gpa and 1.51 Gpa, separately. Al film is a bit harder than TiO_2 film. Finally, the corrosion experiments in simulated body fluid initially indicate the different corrosion properties for Al film and TiO_2 film. Al film presents more effective anti-corrosion properties than TiO_2 film.

Keywords: *Surface properties, Magnesium alloy, Al films, TiO_2 films, Magnetron sputtering*

1. Introduction

For several decades, as excellent light metal and structural materials, magnesium alloys have been widely used in industrial fields such as transportation, building, electronic products, etc[1-8]. Furthermore, because of non-toxic properties and good biocompatibility, magnesium alloys are increasingly focused on the biomedical field[9-11]. However, the surface properties of traditional magnesium alloys are usually unsatisfactory. For example, their anti-corrosion properties are poor, wear resistance is commonplace and and temperature stability is low, which might result in great limitation to their further application[9-13]. Then the surface modification on the magnesium alloys is necessary for improving their properties.

The object of surface modification of magnesium alloys is to prepare one coating layer on the surface. Multiple approaches have been explored to synthesize the coating layer on the surface of magnesium alloy, including anodic or microarc oxidation[3,5,14], magnetron sputtering[4,6], cathodic arc deposition[12], friction stir welding with polymer coating[15], etc. Except magnetron sputtering, the aims of the above techniques are synthesizing compact oxidation layer on the surface of magnesium alloys by means of complicated chemical or electrochemical reaction. So the quality of modification is related to the contents of metal elements and deposition conditions. Comparatively, magnetron sputtering is one kind of physical vapor deposition technique to grow films on substrates, which is convenient and economical for operation with less environmental pollution. There are two working modes for magnetron sputtering. One is dc mode, the other is rf mode. Dc mode is always adopted to deposit metallic films. Rf mode is used for depositing oxide films. Usually the films deposited by magnetron sputtering present good uniformity and desirable properties[4,6].

Due to high hardness and non-toxic properties, TiN film is considered as a competitive coating layer for surface modification on magnesium alloy[11,12]. Furthermore, Al film presents charm for corrosion resistance[4]. Many studies on structural and mechanical properties of Al film and TiN film coated on magnesium alloys were reported[4,16,17]. Considering the biocompatibility of the coating materials in the filed of medical application, TiO_2 film might be also a desirable choice for the modification of magnesium alloy[18]. Then the study on the surface properties of TiO_2 film on magnesium alloy is significant. Additionally, before using as biomedical materials, the degradation mechanism of the coating layers on magnesium alloys should be explored. An effective approach to exploring the degradation mechanism is to study the corrosion behaviors in Hank's simulated body fluid (SBF)[9].

AZ31 is one kind of wrought magnesium alloy, which can be used as the substrates for depositing films. In this paper, the deposition of Al films and TiO_2 films on AZ31 magnesium alloy substrates by means of magnetron sputtering was reported. The surface properties of the films such as

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structure characteristics and corrosion properties in simulated body fluid are explored and compared detailedly.

2. Experimental Procedure

The substrates of the samples are 1 cm × 1 cm as-casted AZ 31 magnesium alloy chips with 2 mm thickness. The chips were firstly ground with SiC abrasive papers and then polished by a mechanical polishing equipment using corundum abrasive. The polished chips were cleaned in acetone by an ultrasonic cleaner, washed by deionized water and finally dried in air.

During the process of magnetron sputtering, the dried AZ31 chips were fixed onto the sample holder in the cavity of the JGP 450 magnetron sputtering equipment, which was manufactured by SKY Technology Development Co., Ltd, Chinese Academy of Sciences. The base pressure of the cavity was 5×10^{-4} Pa, which was measured by a vacuum ionization gauge attached within the JGP450 magnetron sputtering equipment. The substrates were not preheated. For Al samples, the sputtering mode is dc magnetron sputtering. The corresponding sputtering parameters are: 2 inches 99.99% Al disc as target, Ar as working atmosphere with pressure 0.5 Pa, sputtering time 50 minutes, sputtering power 120 W. The Ar flow was maintained as 20 SCCM by a gas flow meter. The Ar working atmosphere pressure was measured by a vacuum resistance gauge also attached within the JGP 450 magnetron sputtering equipment. For TiO_2 samples, the sputtering mode is rf magnetron sputtering. The corresponding sputtering parameters are: 2 inches 99.95% TiO_2 ceramic disc as target, 0.5 Pa working atmosphere mixed with Ar and O_2, sputtering time 55 minutes, sputtering power 150 W.

Firstly, for as-deposited Al film and TiO_2 film samples, the surface morphology was observed by a Shimadz SPM9600 atomic force microscope (AFM) and a Hitachi S-4800 scanning electron microscope (SEM), separately. Secondly, the surface micro-hardness of the as-deposited film sample was measured by a nano-indenter. Thirdly, heat stability experiments for the as-deposited film samples were carried out. The heat treatment process for the samples was: 200°C temperature for 30 minutes and cooling in the air. The surface morphology of the samples after heat treatment was also observed by SEM. Finally, the as-deposited Al film and TiO_2 film samples were separately put into Hank's simulated body fluid (SBF) for the study of corrosion behavior. The composition of SBF was NaCl (8.00g) + KCl (0.40g) + $CaCl_2$ (0.14g) + $NaHCO_3$ (0.35g) + $MgCl_2 \cdot 6H_2O$ (0.1g) + $MgSO_4 \cdot 7H_2O$ (0.06g) + KH_2PO_4 (0.06g) + $Na_2HPO_4 \cdot 12H_2O$ (0.06g) + H_2O (1L). After a few days corrosion, the samples were taken out from the bottles and rinsed by cleaning solution involved with CrO_3 and $AgNO_3$. The surface morphologies of all the corroded samples were characterized by SEM too. In addition, the corrosion experiments in SBF were also conducted to the bare AZ31 magnesium alloy substrates for the sake of comparing the corrosion properties between the coating layers and the substrates.

3. Result and discussion

The as-deposited TiO_2 films on the AZ31 magnesium alloys look bright and the as-deposited Al films present light grey. The thickness of the as-deposited films is about 3 μm, estimated from the section morphologies of the films observed by SEM. X-ray diffraction (XRD) spectra of the samples reveal obvious polycrystalline structural characteristics. Figure 1 shows the XRD spectra of the as-deposited Al film and TiO_2 film samples. The diffraction peaks of magnesium alloy substrates are much stronger. However, some peaks of Al film and TiO_2 film can still be distinguished. For Al film, the peaks are corresponding to the (111), (200) and (220) crystal plane diffraction of face centered cubic Al. For TiO_2 film, two anatase peaks corresponding to (101) and (200) crystal plane diffraction are displayed, which reveals that the TiO_2 film is mainly composed of anatase phases. This result should be ascribed to low deposition temperature of the film.

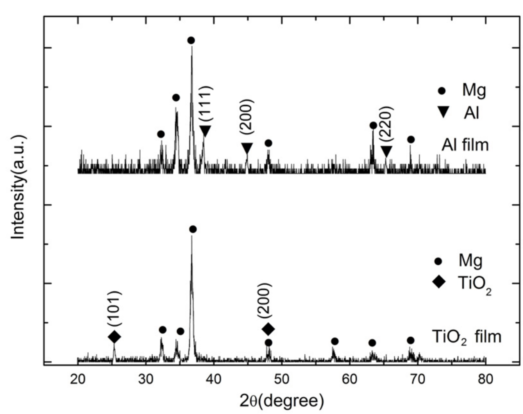

Figure 1. The XRD spectra of as-deposited Al film and TiO_2 film samples.

The surface morphologies of the as-deposited Al film and TiO_2 film observed by AFM are shown by Figure 2. The AFM photos distinctly reveal that both of the two films presents flat surface. The root mean square roughness of Al film and TiO_2 film is about 10 nm and 9 nm, respectively, implying that the crystallizing grains of Al film is a bit larger than those of TiO_2 film. These facts are further demonstrated by SEM photos of the samples displayed by Figure 3. At the same time, Figure 3 exhibits the similar surface characteristics for the two samples. Whether for Al film or TiO_2 film, the grains were uniform and the surface looks compact. There are not structural defects including cracks or holes. Wu et al. studied the microstructure of Al film coated on AZ91D magnesium alloy by magnetron sputtering and also observed that there were no cracks on the surface of Al film.[4] They ascribed the compact structure characteristics to the similar thermal expansion coefficient between the AZ91D substrate and pure Al. Thus we deduce that for our samples, the coefficient of thermal expansion of AZ31 magnesium alloy, Al and TiO_2 might also be similar.

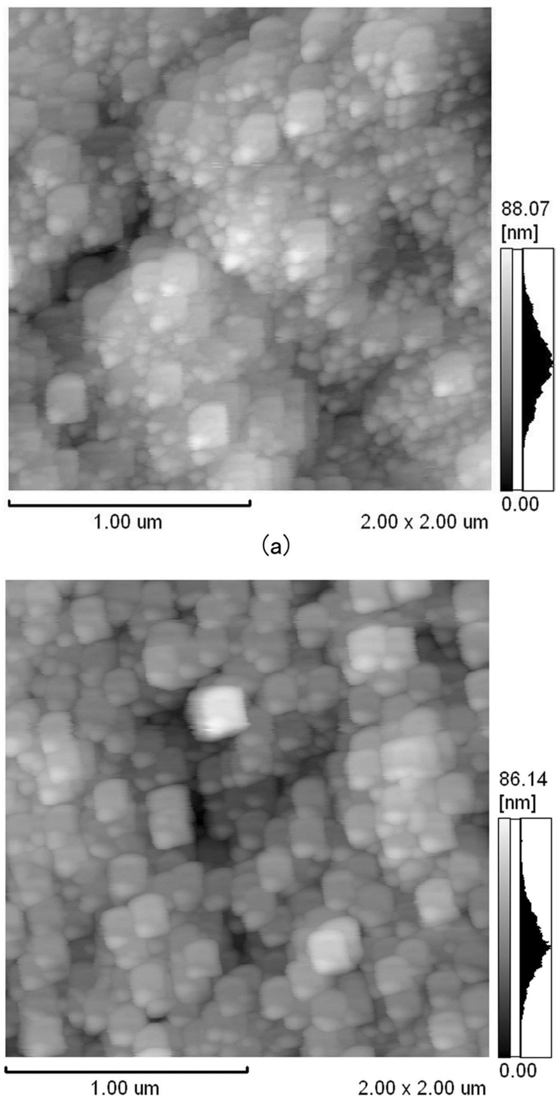

Figure 2. The surface morphology images of as-deposited films observed by AFM (a: Al film. b: TiO_2 film).

Figure 4 displays the SEM photos of the surfaces of Al film and TiO_2 film samples after heat treatment under the heat technique mentioned above. Compared to the surface structural characteristics before heat treatment, for Al film sample, the grains become slightly smaller, implying that recrystallization might occur. However, for TiO_2 film, the size of the grains hardly changes. In addition, no defects such as cracks are observed on the surface of the samples and the surface keeps compact after heat treatment, indicating

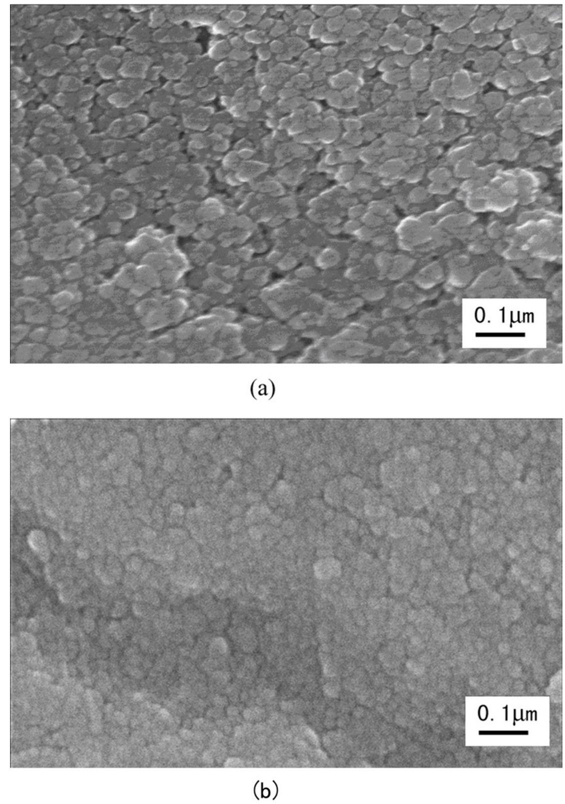

Figure 3. The surface morphology images of as-deposited films observed by SEM (a: Al film. b: TiO_2 film).

that the films have good heat stability of structure, although the samples suffered from fast cooling process in air. These phenomena might also result from the similar coefficient of thermal expansion of AZ 31 magnesium alloy, Al and TiO_2, as discussed above.

For investigating the micro-hardness properties of the whole surface of the film samples, 16 indentation points were adopted. The range of micro-hardness values is 1.49 Gpa -2.38 Gpa for Al film sample and 1.14 Gpa - 2.07 Gpa for TiO_2 film. The corresponding arithmetic average value of the hardness of the 16 points is 1.90 Gpa for Al film and 1.51 Gpa for TiO_2 film. Thus Al film is a bit harder than TiO_2 film. However, the micro-hardness of either Al film or TiO_2 film is much lower than that of TiN film by one order of magnitude, meaning that Al film and TiO_2 film have lower wear resistance than TiN film [4,16,17].

Figure 5 exhibits the surface and section morphologies of bare AZ 31 magnesium alloy substrates without coating layer after corrosion experiment in SBF. Here, the corrosion period is separately 3 days, 10 days and 15 days. Figure 5 (a1) and Figure 5 (a2) correspond to the surface and section SEM morphologies of the sample after 3 days corrosion, respectively. Similarly, Figure 5 (b1) and Figure 5(b2) correspond to the condition of 10 days corrosion. Figure 5(c1) and Figure 5 (c2) correspond to the condition of 15 days corrosion. As shown

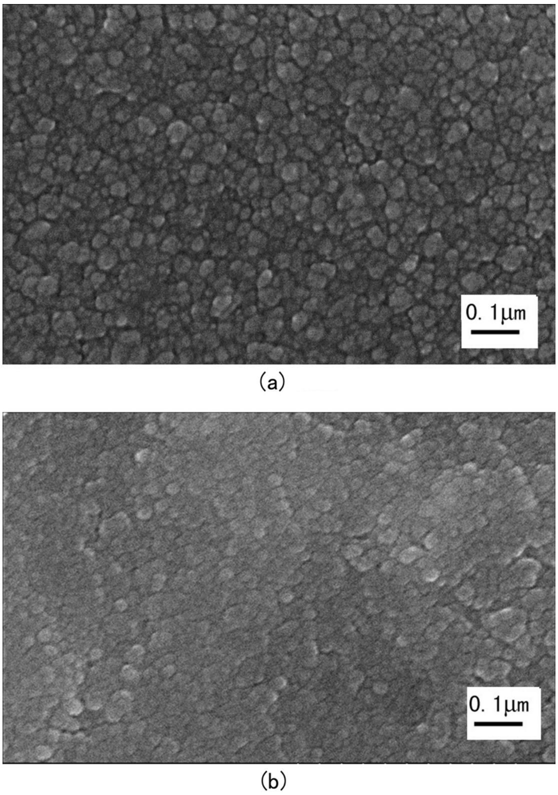

Figure 4. The surface morphology images of the films observed by SEM after heat treatment (a: Al film. b: TiO_2 film).

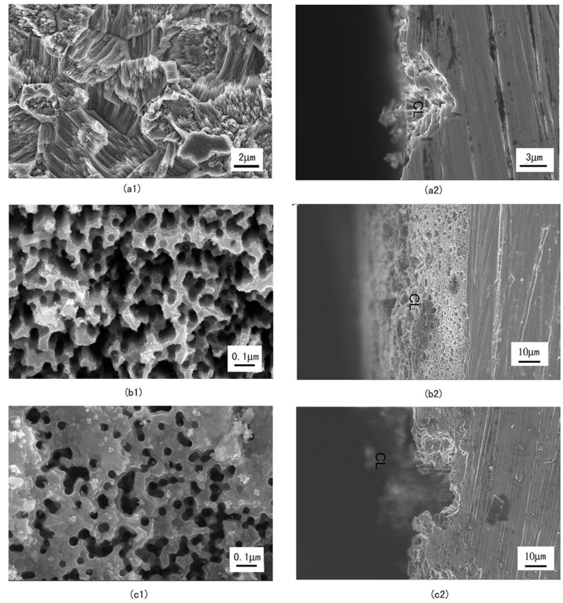

Figure 5. The surface and section morphology images of AZ31 magnesium alloy substrate observed by SEM after corrosion experiment in SBF (a, b and c are corresponding to 3 days, 10 days and 15 days corrosion, respectively. The left column of the figure is corresponding to surface morphology and the right column corresponding to section morphology).

in Figure 5 (a1) and Figure 5 (a2), after 3 days immersion in SBF, the crystalline structure of the magnesium alloys was destroyed under the action of SBF. Corrosion near crystalline borders is obvious. Some corrosion holes were distributed in the corrosion layer (CL). The depth of the corrosion hole is about 6 μm. After a longer corrosion time such as 10 days and 15 days, the surface of the magnesium alloy sample became wholly porous. The depth of the CL is beyond 30 μm. Even under the condition of 15 days corrosion, deeper corrosion holes appeared. These phenomena indicate the poor anti-corrosion properties of AZ31 magnesium alloys in SBF. Wang et al. studied the electrochemical corrosion behavior of bare AZ91 magnesium alloys in SBF and reported the high absolute corrosion potential of AZ91 magnesium alloys and corrosion current density[19]. For our work, although the electrochemical polarization was not carried out, it could still be deduced that AZ31 magnesium would also present high absolute corrosion potential, which is responsible for the poor anti-corrosion properties in SBF.

Additionally, the magnesium corrosion reaction could be formulated by the electrochemical equation as follow[20]:

$$Mg + H_2O \rightarrow Mg^{2+} + 2OH^- + H_2$$

It is known that the formation of OH^- ions and gaseous hydrogen may be harmful to the life tissue[20]. Simultaneously considering the poor anti-corrosion properties, thus the bare magnesium alloys is not proper to used as biomedical materials.

The surface and section morphologies of Al film samples after certain corrosion procedure in SBF are shown in Figure 6. The corrosion time is also chosen as 3 days, 10 days and 15 days, separately. As shown in Figure 6 (d1) and Figure 6 (d2), after 3 days immersion in SBF, the compact structure of the film is lightly destroyed. The CL is not obvious. Thus the magnesium alloy substrate is prevented by Al film from corrosion within 3 days. However, after 10 days corrosion in SBF, many corrosion holes appeared. As displayed in Figure 6 (e2), the depth of the holes is less than 3 μm. Because the depth of as-deposited Al film is about 3 μm, it could be deduced that the Al film could still prevent the substrate from corrosion within 10 days in SBF. Finally, after 15 days corrosion in SBF, the whole surface of the sample became a CL. The depth of the CL is beyond 10 μm, meaning that the substrate itself also suffered from corrosion to some degree.

According to other reports about corrosion experiments of Al film in single metal salt solutions such as NaCl, a Al_2O_3 layer was always observed on the surface of Al film, implying passivation behavior of Al film, which would lower the corrosion speed of the film.[21,22] In our work, the SBF contains multiple metal salts and passivation behavior would also occur for Al film, which would help the magnesium alloy substrate to avoid corroding in several days. However, with the time of sample immersion in BSF being increased to more days, the CL becomes obvious, indicating that the passivation layer was destroyed.

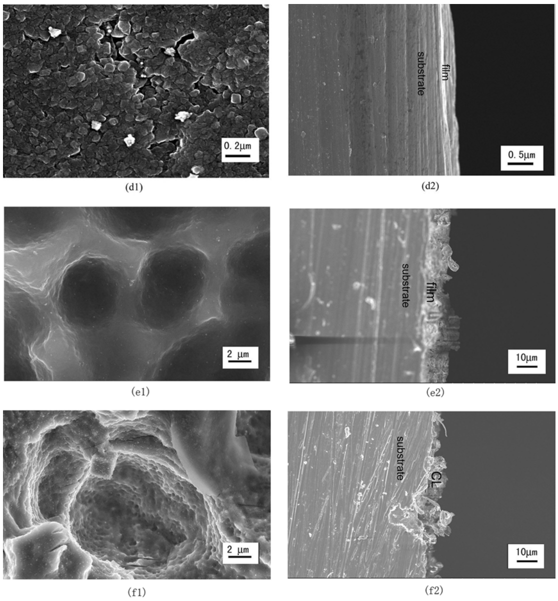

Figure 6. The surface and section morphology images of Al film samples observed by SEM after corrosion experiment in SBF (d, e and f are corresponding to 3 days, 10 days and 15 days corrosion, respectively. The left column of the figure is corresponding to surface morphology and the right column corresponding to section morphology).

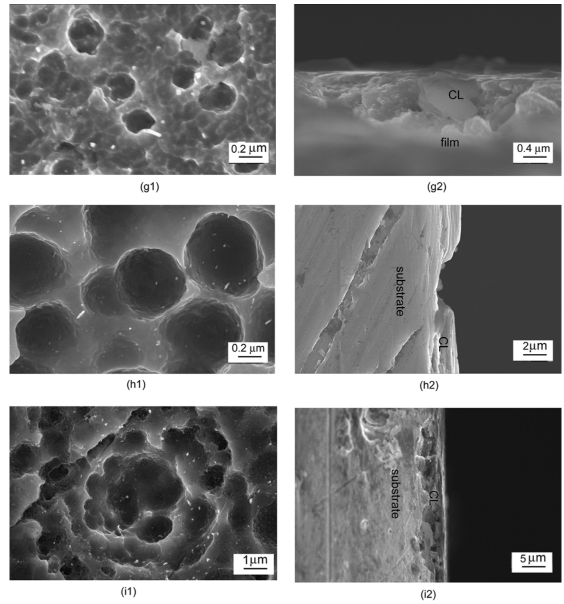

Figure 7. The surface and section morphology images of TiO_2 film samples observed by SEM after corrosion experiment in SBF (g, h and i are corresponding to 3 days, 7 days and 10 days corrosion, respectively. The left column of the figure is corresponding to surface morphology and the right column corresponding to section morphology).

For TiO_2 film sample, the surface and section morphologies after corrosion experiment in SBF are shown in Figure 7. Here, the corrosion time is a bit different from that of Al film, which was chosen as 3 days, 7days and 10 days, respectively. Unlike the conditions of Al film samples, firstly, as shown in Figure 7 (g1) and Figure 7 (g2), after 3 days immersion in SBF, the compact structure of the TiO_2 film is heavily destroyed. The corrosion holes appeared earlier, compared to the condition of Al film. However, the depth of the corrosion holes is less than 2 μm. Because the thickness of as-deposited TiO_2 film is about 3 μm, it could be referred that the magnesium alloy substrate was prevented from corrosion by TiO_2 film within 3 days. Wang et al studied the corrosion behavior of microarc oxidation layer including TiO_2 on AZ91 magnesium alloy substrates in SBF. They found that the microarc oxidation layer including TiO_2 presented lower absolute corrosion potential than the bare AZ91 magnesium alloys and its corrosion current density was lower than the bare AZ91 magnesium alloys by two orders of magnitude. Thus the microarc oxidation layer would prevent the AZ91 magnesium alloy substrates from suffering from corrosion in SBF in limited time. Similarly it could be deduced that the TiO_2 film on AZ31 magnesium alloys should have lower absolute corrosion potential and corrosion current density than bare AZ 31 magnesium alloys, which was responsible for the improved the anti-corrosion properties of the sample in SBF.

Secondly, after 7 days immersion in SBF, the corrosion holes became larger and the depth of the holes exceeded 3 μm, indicating that the substrate began to be corroded. Thirdly, after 10 days immersion in SBF, the whole surface of TiO_2 film became one CL with depth beyond 6 μm. At the same time the magnesium alloy substrate suffered from heavier corrosion. However, compared to the condition of bare substrate, the corrosion degree is much lower for TiO_2 film within 10 days corrosion in SBF.

In general, according to the above experiment results, the bare magnesium alloy substrates present poor anti-corrosion properties in SBF. Both Al film and TiO_2 film could hinder the corrosion to the magnesium alloy substrates in SBF within some days. But the hindering time for Al film is over 10 days, longer than 7 days for TiO_2 film. This means that Al film presents lower corrosion rate than TiO_2 film. These results should be related to the corrosion mechanism. For Al film, there exists passivation behavior. However, for TiO_2 film, the passivation behavior would not appear in SBF.

The corrosion behavior of surface-modified magnesium alloy could be further understood as degradation behavior. Based on the above results and discussions, it could be concluded that the degradation properties of magnesium alloys could be adjusted by using proper coating layer, which is vital to clinical application.

4. Conclusions

As-deposited Al films and TiO_2 films on AZ 31 magnesium alloy substrates were prepared by magnetron sputtering and present compact structure characteristics. The heat treatment under 200°C for 30 minutes could not destroy the compact structure characteristics of the samples. No cracks or holes appeared on the surface of the samples, revealing the thermal stability of structure of the samples. Nano-indentation measurement shows that Al film is a bit harder than TiO_2 film.At last the corrosion experiments in simulated body fluid initially reveal different corrosion behaviors between Al film and TiO_2 film. Al film presents more effective anti-corrosion properties in SBF than TiO_2 film. Al film could prevent magnesium alloy substrate from corrosion within 10 days, which is longer than 7 days for TiO_2 film. These results would be helpful for exploring the application of magnesium alloy on biomedical field.

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